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(54) Composition comprising 1,1,1,3,3-pentafluorobutane, methylene chloride and methanol, for the cleaning and/or drying of solid surfaces

(57) A cleaning composition comprises, by weight, 30 to 69 % 1, 1, 1, 3, 3-pentafluorobutane (F365-mfc), 30 to 60 % methylene chloride and 1 to 10 % methanol, which compounds form a positive azeotrope (B.p. = 32.1° C at normal pressure). The composition, optionally stabilised, may be used for the cleaning and/or the drying of solid surfaces, in particular for removing flux from printed circuits and for degreasing mechanical components.

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COMPOSITION BASED ON 1,1,1,3,3-PENTAFLUOROBUTANE, METHYLENE CHLORIDE AND METHANOL, FOR THE CLEANING AND/OR DRYING OF SOLID SURFACES

The present invention relates to a fluorinated hydrocarbon-containing composition which can be used in the applications of drying, cleaning, degreasing and drycleaning solid surfaces, in particular in the removal of flux and the cold cleaning of printed circuits.

1,1,2-Trichloro-1,2,2-trichloroethane (known in the profession under the name F113) is widely used in industry for the cleaning and degreasing of solid surfaces. Besides its application in electronics to the cleaning of solder fluxes in order to remove the surface-attacking flux which adheres to printed circuits, there may be mentioned its applications to the degreasing of heavy-metal components and to the cleaning of mechanical components of high quality and high precision, such as, for example, gyroscopes and military or aerospace equipment. In its various applications, F113 is most often combined with other organic solvents (for example methanol), preferably in the form of azeotropic or pseudoazeotropic mixtures which do not demix and which, used at reflux, have substantially the same composition in the vapour phase as in the liquid phase.

However, F113 is one of the completely halogenated chlorofluorocarbons which are currently suspected of attacking or damaging stratospheric ozone.

In order to contribute to solving this problem, the

present invention proposes to replace the F113-based compositions by a new composition based on methylene chloride, methanol and 1,1,1,3,3-pentafluorobutane. The latter compound, known in the profession under the name F365-mfc, has no destructive effect with respect to ozone (ODP = 0).

According to the present invention there is provided a composition which comprises from 30 to 69 % by weight F365-mfc, from 30 to 60 % methylene chloride and from 1 to 10 % methanol. Within the ranges specified, there exists an azeotrope whose boiling temperature is 32.1°C at normal atmospheric pressure (1.013 bar) and the composition according to the invention has a pseudoazeotropic behaviour, that is to say the composition of the vapour and liquid phases is substantially the same, which is particularly advantageous for the applications envisaged. Preferably, the F365-mfc content is chosen between 49 and 61 % by weight, that of methylene chloride between 37 and 46 % by weight and that of methanol between 2 and 5 % by weight.

The composition according to the invention additionally has the significant advantage of not exhibiting an ignition point under the standard determination conditions (ASTM standard D-3828); the composition is thus nonflammable.

The F365-mfc/methylene chloride/methanol azeotrope is a positive azeotrope since its boiling point (32.1°C) is less than those of the three constituents (F365-mfc: 40°C; methylene chloride: 40°C; methanol: 65°C).

As in the known F113-based compositions, the composition according to the invention can advantageously be stabilised against hydrolysis and/or free-radical attacks which are capable of taking place in the cleaning processes by adding thereto a conventional stabilising agent such as, for example, a nitroalkane, an epoxide or a mixture of such compounds, it being possible for the proportion of stabilising agent to range from 0.01 to 5 % with respect to the total F365-mfc + methylene chloride + methanol weight.

The composition according to the invention can be used in the same applications and according to the same techniques as the prior F113-based compositions.

The following Examples further illustrate the present invention without limiting it.

EXAMPLE 1: DISCLOSURE OF THE AZEOTROPE

100 g of methylene chloride, 50 g of methanol and 100 g of F365-mfc are introduced into the distillation flask of a distillation column (30 plates). The mixture is then put on total reflux for one hour to bring the system to equilibrium. At the temperature plateau (32.1°C), a fraction (approximately 50 g) is withdrawn and analysed by gas phase chromatography.

Examination of the results, recorded in the table below, indicates the presence of a F365-mfc/methylene chloride/methanol azeotrope.

	COMPOSITION (% BY WEIGHT)		
	P365-mfc	CH_2Cl_2	Methanol
Initial mixture	40	40	20
Withdrawn fraction	57	39.5	3.5

EXAMPLE 2: VERIFICATION OF THE AZEOTROPIC COMPOSITION

200 g of a mixture containing, by weight, 57 % P365-mfc, 39.5 % methylene chloride and 3.5 % methanol are introduced into the distillation flask of an adiabatic distillation column (30 plates). The mixture is then brought to reflux for one hour to bring the system to equilibrium, then a fraction of approximately 50 g is drawn off and analysed, as are the distillation bottoms, by gas phase chromatography. The results recorded in the following table show the presence of a positive azeotrope since its boiling point is less than those of the pure constituents: P365-mfc, methylene chloride and methanol.

	COMPOSITION (% by weight)		
	P365-mfc	CH_2Cl_2	Methanol
Initial mixture	57	39.5	3.5
Fraction collected	57	39.5	3.5
Distillation bottoms	57	39.5	3.5
Boiling temperature corrected for 1.013 bar: 32.1°C			

This azeotrope, used for the cleaning of solder flux or in the degreasing of mechanical components, gives results which are as good as those given by the compositions based on F113 and methanol.

EXAMPLE 3: COMPOSITION STABILISED BY NITROMETHANE

150 g of a mixture containing, by weight, 57 % P365-mfc, 39.4 % methylene chloride, 3.5 % methanol and 0.1 % nitromethane as stabilising agent are introduced into an ultrasound cleaning vessel. After the system has been put on reflux for one hour, an aliquot of the vapour phase is withdrawn. Its analysis by gas phase chromatography shows the presence of nitromethane, which indicates that the mixture is stabilised in the vapour phase.

	COMPOSITION (% by weight)			
	F365-mfc	CH_2Cl_2	Methanol	CH_3NO_2
Initial mixture	57	39.4	3.5	0.1
Vapour phase	57	39.5	3.49	0.01

EXAMPLE 4: COMPOSITION STABILISED BY PROPYLENE OXIDE

If Example 3 is repeated, replacing nitromethane by propylene oxide, the following results are obtained:

	COMPOSITION (% by weight)			
	F365-mfc	CH_2Cl_2	Methanol	C_3H_6O
Initial mixture	57	39.4	3.5	0.1
Vapour phase	57	39.5	3.48	0.02

EXAMPLE 5: CLEANING OF SOLDER FLUX

200 g of the F365-mfc/methylene chloride/methanol azeotropic composition are introduced into an Annemasse ultrasound vessel, and then the mixture is brought to boiling temperature.

Standard circuits (IPC-B-25 model), coated with solder flux and annealed in an oven for 30 seconds at 220°C,

are immersed for 3 minutes in the liquid at boiling point under ultrasound, and then rinsed in the vapour phase for 3 minutes.

After drying in air, viewing in oblique light shows the complete absence of solder flux residue.

CLAIMS

1. A composition comprising, by weight, from 30 to 69 % 1,1,1,3,3-pentafluorobutane, from 30 to 60 % methylene chloride and from 1 to 10 % methanol.

2. A composition according to Claim 1, containing, by weight, from 49 to 61 % 1,1,1,3,3-pentafluorobutane, from 37 to 46 % methylene chloride, and from 2 to 5 % methanol.

3. A composition according to Claim 2, in the form of an azeotrope boiling at 32.1°C at normal pressure.

4. A composition according to any one of Claims 1 to 3, which additionally comprises at least one stabilising agent.

5. A composition according to Claim 4, in which the stabilising agent is a nitroalkane, an epoxide or a mixture thereof.

6. A composition according to Claim 4 or 5, in which the proportion of stabilising agent is from 0.01 to 5 % with respect to the total weight of the 1,1,1,3,3-pentafluorobutane + methylene chloride + methanol mixture.

7. A composition according to claim 1 substantially as described in the Examples.

8. Use of a composition as claimed in any one of Claims 1 to 7 for cleaning and/or drying of a solid surface.

9. Use according to Claim 8 for removal of flux from a printed circuit or degreasing of mechanical

components.

10. A method of drying, cleaning, degreasing or drycleaning a solid surface which method comprises applying to the solid surface a composition as claimed in any one of claims 1 to 7.

11. A method according to claim 10 wherein flux is removed from a printed circuit or mechanical components are degreased.

Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9317312.8
Relevant Technical Fields (i) UK Cl (Ed.L) C5D (DAA) (ii) Int Cl (Ed.5) C11D 7/60, 7/50	Search Examiner C SHERRINGTON Date of completion of Search 13 DECEMBER 93
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: WPI, CLAIMS	Documents considered relevant following a search in respect of Claims :- 1-11

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
P X	WPI Abstract Accession No. 93-253064/32 and JP 510071190 A (ASAHI GLASS CO LTD)	1-11

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